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(71)Applicant : KANSAI SHINGIJUTSU KENKYUSHO:KK
(72)Inventor : ASAKUMA NAOKO
IMAI HIROAKI

(54) PRODUCTION OF METALLIC OXIDE THIN FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method capable of forming thin film of crystallized transition metal oxide even on a substrate low in heat resistance such as plastics, free from the need of the use of expensive producing equipment and free from restriction by the shape and size of a substrate to be film-formed.
SOLUTION: The surface of the object to be coated is coated with a precursory coating soln. of metallic oxide obtd. by using the alkoxide of salt of transition metal as a starting raw material to form coating film on the surface of the object to be coated, and thereafter, the coating film is irradiated with ultraviolet light of ≥360 nm wavelength to crystallize the transition metal oxide forming the coating film.

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(71)出願人　５９１１６７４３０
株式会社関西新技術研究所
大阪府大阪市中央区平野町４丁目１－２

(72)発明者　朝隈　直子
京都府乙訓郡大山崎町円明寺脇山１－１２０

(72)発明者　今井　宏明
東京都板橋区小茂根１－１０－１７

(74)代理人　弁理士　間宮　武雄

(54)【発明の名称】金属酸化物薄膜の製造方法

(57)【要約】
【課題】　プラスチックスなどの耐熱性の低い基体上にも、結晶化した遷移金属酸化物の薄膜を形成でき、高価な製造設備を使用する必要も無く、成膜しようとする基体の形状や大きさにも制約されない方法を提供する。
【解決手段】　遷移金属のアルコキシドまたは塩を出発原料として得られる金属酸化物の前駆体塗布液を被塗布物の表面に塗布して、被塗布物表面に塗布膜を形成した後、その塗布膜に対して波長が３６０ｎｍ以下である紫外光を照射し、塗布膜を形成している遷移金属酸化物を結晶化させる。

【特許請求の範囲】

【請求項1】　遷移金属のアルコキシドまたは塩を出発原料として得られる金属酸化物の前駆体塗布液を被塗布物の表面に塗布して、被塗布物表面に塗布膜を形成した後、その塗布膜に対して波長が360nm以下である紫外光を照射し、塗布膜を形成している遷移金属酸化物を結晶化させることを特徴とする、金属酸化物薄膜の製造方法。

【請求項2】　遷移金属が、IVa族元素またはVa族元素である請求項1記載の、金属酸化物薄膜の製造方法。

【請求項3】　塗布膜に対して照射する紫外光の光源が、高圧水銀ランプ、低圧水銀ランプ、ArFエキシマレーザ、KrFエキシマレーザ、YAGレーザの4倍波もしくは3倍波、エキシマランプまたはシンクロトロン放射光である請求項1または請求項2記載の、金属酸化物薄膜の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、ガラス、セラミックス、金属、プラスチックス等の基板の表面に電子材料などの機能性酸化物薄膜を形成する方法、特に、加熱処理することなく結晶化された遷移金属酸化物の薄膜を形成する金属酸化物薄膜の製造方法に関する。

【0002】

【従来の技術】遷移金属酸化物には、誘電材料、導電材料、半導体材料などとして優れた電気特性を有する化合物が多く存在する。これら遷移金属酸化物の薄膜は、ゾル－ゲル法、噴霧熱分解法、スパッタリング法、MOCVD法などにより製造される。

【0003】ゾル－ゲル法による遷移金属酸化物薄膜の製造方法に関しては、例えば、チタニア膜は、400℃の温度でアナターゼが結晶化し、さらに800℃の温度で加熱処理することによりルチル相へ転移することが知られており、ジルコニア膜は、700℃の温度で加熱処理することにより結晶化し（窯業協会誌、94、823（1986）参照）、酸化ニオブ膜は、400℃の温度で加熱処理することにより結晶化し（キャタリシス・トゥデイ（Catalysis Today）、16、495（1993）参照）、酸化鉄膜は、450℃までの温度でγ－酸化鉄（ヘグマタイト）へ結晶化し、さらに450℃以上の温度で加熱処理することによりα－酸化鉄へ転移し（ジャーナル・オブ・マテリアル・サイエンス（J. Mater. Sci.）、26、497（1991）参照）、酸化亜鉛膜は、400℃以上の温度で結晶化すること（日本セラミックス協会学術論文誌、104、296（1991）参照）がそれぞれ報告されている。また、噴霧熱分解法による遷移金属酸化物薄膜の製造方法に関しては、各種の金属塩を出発原料として酸化鉄、クロミア、チタニア、ジルコニアなどの薄膜が形成されることが報告されている（チン・ソリッド・フィルムズ（Thin Solid Films）、77、81（1981）参照）。

【0004】

【発明が解決しようとする課題】上記したように、一般的なゾル－ゲル法や噴霧分解法により遷移金属酸化物の薄膜を形成する従来方法では、残留有機物や金属塩を熱分解して除去することが必要であり、その結果として、金属酸化物を結晶化させるためには、400℃以上の高温での加熱処理が必須である。このため、従来の方法によっては、プラスチックスなどのような耐熱性の低い基体上に、結晶化した遷移金属酸化物の薄膜を形成することができなかった。

【0005】また、スパッタリング法やMOCVD法は、真空プロセスによるものであり、このため、高価な製造設備が必要で、製造コストが高くなり、また、成膜しようとする基体の形状や大きさに制約がある、といった問題点がある。また、これらの方法も、結晶性の金属酸化物薄膜を得るためには、基板の加熱処理を必要とする場合が多い。

【0006】この発明は、以上のような事情に鑑みてなされたものであり、プラスチックスなどの耐熱性の低い基体上にも、結晶化した遷移金属酸化物の薄膜を形成することができ、高価な製造設備を使用する必要も無く、また、成膜しようとする基体の形状や大きさにも制約されない金属酸化物薄膜の製造方法を提供することを目的とする。

【0007】

【課題を解決するための手段】この発明では、上記目的を達成するための手段として、ゾル－ゲル法により形成された遷移金属酸化物ゲルの薄膜を結晶化させるのに、紫外光を利用するようにした。すなわち、請求項1に係る発明は、遷移金属のアルコキシドまたは塩を出発原料として得られる金属酸化物の前駆体塗布液を被塗布物の表面に塗布して、被塗布物表面に塗布膜を形成した後、その塗布膜に対して波長が360nm以下である紫外光を照射し、塗布膜を形成している遷移金属酸化物を結晶化させることを特徴とする。

【0008】請求項1に係る発明の製造方法では、遷移金属のアルコキシドまたは塩を出発原料として得られる金属酸化物の前駆体塗布液を被塗布物の表面に塗布して、塗布膜を形成した後、その塗布膜に対して波長が360nm以下である紫外光を照射することにより、遷移金属酸化物が結晶化される。したがって、遷移金属酸化物の結晶化のために高温での加熱処理を行う必要が無いので、プラスチックスのような耐熱性の低い基体上にも、結晶化した遷移金属酸化物の薄膜を形成することが可能になる。なお、紫外光の照射による遷移金属酸化物の結晶化のメカニズムは明確ではないが、紫外光を薄膜が吸収し、そのエネルギーによって原子の再配列が進行させられ、遷移金属酸化物が結晶化するものと考えられ

る。

【0009】請求項2に係る発明は、請求項1記載の製造方法において、遷移金属がIVa族元素またはVa族元素であることを特徴とする。

【0010】請求項3に係る発明は、請求項1または請求項2記載の製造方法において、金属酸化物ゲルの薄膜に対して照射する紫外光の光源として、高圧水銀ランプ、低圧水銀ランプ、ArFエキシマレーザ、KrFエキシマレーザ、YAGレーザの4倍波もしくは3倍波、エキシマランプまたはシンクロトロン放射光を使用することを特徴とする。光源は、1種類のものだけを使用しても、また2種以上のものを組み合わせて使用してもよい。

【0011】

【発明の実施の形態】以下、この発明の好適な実施形態について説明する。

【0012】この発明に係る金属酸化物薄膜の製造方法では、まず、遷移金属のアルコキシドまたは塩を出発原料として、金属酸化物の前駆体塗布液（ゾル）を調製する。遷移金属は、例えばIVa族元素またはVa族元素である。塗布液の調製方法は特に限定されないが、塗布膜（ゲル膜）を形成したときに、膜中の残留有機物が少なくなる程、また、加熱処理によるゲル膜の結晶化温度が低くなる程好ましい。塗布液の調製方法を以下に説明する。

【0013】出発原料として使用される金属アルコキシドとしては、アルコキシル基の炭素数が1～5であるものが使用され、より好ましくはアルコキシル基の炭素数が2～4のものが使用される。また、金属塩としては、硝酸塩、塩化物などの無機塩、酢酸などの有機酸塩や、アセチルアセトナートなどのβ－ジケトンの塩が使用される。

【0014】金属アルコキシドまたは金属塩を溶解させる溶剤としては、メタノール、エタノール、プロパノール、ブタノールなどのアルコール類、酢酸エチルなどの有機酸エステル、アセトニトリル、アセトンやメチルエチルケトンなどのケトン類、テトラヒドラフラン（THF）やジオキサンなどのシクロエーテル、ホルムアミド（FA）、N，N－ジメチルホルムアミド（DMF）などの酸アミド、炭化水素、トルエンなどの芳香族などが使用される。

【0015】また、金属アルコキシドを含む溶液に、多座配位化合物であるβ－ジケトン（$RCOCH_2COR'$；R、R'はアルキル基またはアルコキシル基）、アルコキシアルコール、アルカノールアミン、グリコール類、グリセリンなどを、アルコキシドの安定化の目的で含まれるようにしてもよい。β－ジケトンとしては、アセチルアセトン、アセト酢酸エチルやアセト酢酸メチルなどのアセト酢酸エステル、マロン酸ジエチルなどのマロン酸エステルなどが使用される。アルコキシアルコールとしては、2－メトキシエタノール、2－エトキシエタノール、2－メトキシ－2－プロパノールなどが使用される。アルカノールアミンとしては、モノエタノールアミン、ジエタノールアミン、トリエタノールアミンなどが使用される。グリコール類としては、エチレングリコール、ジエチレングリコール、トリエチレングリコールおよびプロピレングリコールやこれらの化合物のモノアルキルエーテルや酢酸エステルが使用される。これらの化合物は単独で用いられあるいは併用され、その種類は、金属種やアルコキシル基の種類により選定される。また、これらの化合物は、アルコキシドの0．1モル倍～1．5モル倍の量が含まれることが望ましい。なお、アルコキシアルコール類は、溶媒として使用することも可能である。

【0016】金属アルコキシドまたは金属塩を含む溶液の加水分解には、金属アルコキシドまたは金属塩の0．05モル倍～2モル倍の水が用いられ、より好ましくは、0．5モル倍～1．5モル倍の水が用いられる。この加水分解には、酸触媒および／または塩基触媒を用いるようにしてもよく、好ましくは、塩酸などの鉱酸や酢酸などの有機酸が用いられる。なお、アルコキシドの種類によっては、アルコキシドの希釈溶液が用いられる。また、出発原料として金属塩を使用した場合には、アルコール系の溶剤との反応を有効に利用するようにする。

【0017】遷移金属のアルコキシドまたは塩を含む溶液の加水分解によって金属酸化物の前駆体塗布液（ゾル）が調製されると、その塗布液を基板の表面に塗布し、それを乾燥させて基板表面に塗布膜（金属酸化物ゲル膜）を形成する。塗布液の塗布方法は、特に限定されず、通常行われるディップコート法、スピンコート法、フローコート法、バーコート法、超音波噴霧法などが用いられる。なお、このとき得られたゲル膜としては、上記したように、その膜中の残留有機物量が少ない程、また、加熱処理した場合の結晶化温度が低い程好ましい。

【0018】基板表面に塗布膜が形成されると、その塗布膜に対して波長が360nm以下である紫外光を照射する。紫外光の光源としては、波長が360nm以下である紫外光を照射可能であれば、その種類を問わず、目的とする金属酸化物薄膜に応じて適宜選択して使用されるが、例えば、高圧水銀ランプ、低圧水銀ランプ、エキシマランプ、ArFエキシマレーザ、KrFエキシマレーザ、YAGレーザ4倍波または3倍波、シンクロトロン放射光などが使用される。また、これらの光源のうち2つもしくはそれ以上のものを組み合わせて使用することも可能である。この塗布膜に対する紫外光照射の際に、目的に応じて、基板を加熱したり、基板を減圧下に置いたり、雰囲気（酸化雰囲気または非酸化雰囲気）を制御したりすることも可能である。また、紫外光の照射強度やショット数は、塗布膜の種類や組成などに応じて適宜選択される。塗布膜に対して紫外光が照射されるこ

とにより、塗布膜を形成している金属酸化物ゲルが結晶化され、基板の表面に遷移金属酸化物の薄膜が形成される。

【0019】

【実施例】次に、この発明を具体的に適用した実施例について説明する。

【0020】〔実施例1〕ペンタエトキシタンタルを、金属酸化物の固形分濃度が3重量％となるようにエタノールに溶解させて、塗布液を調製した。この塗布液を、スピンコータ（2，000rpm×15秒）を使用してシリカ基板上に塗布した後、100℃の温度の乾燥器で1時間乾燥させて、シリカ基板上に塗布膜を形成した。得られた塗布膜に、ArFエキシマレーザ（193nm、25mJ／cm^2、300ショット）を照射した。これにより、結晶性の酸化タンタル（Ta_2O_5）薄膜が得られた。得られた薄膜の薄膜X線回折パターンを図1に示す。

【0021】〔実施例2〕ペンタエトキシニオブを、金属酸化物の固形分濃度が3重量％となるようにエタノールに溶解させて、塗布液を調製した。この塗布液を、スピンコータ（2，000rpm×15秒）を使用してシリカ基板上に塗布した後、100℃の温度の乾燥器で1時間乾燥させて、シリカ基板上に塗布膜を形成した。得られた塗布膜に、ArFエキシマレーザ（193nm、25mJ／cm^2、300ショット）を照射した。これにより、結晶性の酸化ニオブ（Nb_2O_5）薄膜が得られた。

【0022】〔実施例3〕テトライソプロポキシチタンを2－メトキシエタノールに溶解させ、チタンと等モルの水を含む0．1規定塩酸を2－メトキシエタノール溶液に添加し、溶液を加水分解させて、塗布液を調製した。この塗布液中の金属酸化物の固形分濃度は、3重量％となるようにした。この塗布液を、スピンコータ（2，000rpm×15秒）を使用してシリコン基板上に塗布した後、100℃の温度の乾燥器で1時間乾燥させて、シリコン基板上に塗布膜を形成した。得られた塗布膜に、YAGレーザの4倍波（266nm、10mJ／cm^2）を、照射ショット数を変化させて照射した。これにより、ルチル（TiO_2）薄膜が得られた。照射ショット数が100ショットであったときに、ルチル回折ピークが認められた。得られた薄膜の薄膜X線回折パターンの変化を図2に示す。

【0023】〔実施例4〕四塩化チタンを、金属酸化物の固形分濃度が3重量％となるように無水エタノールに添加し、1日撹拌して溶解させ、塗布液を調製した。この塗布液を、スピンコータ（2，000rpm×15秒）を使用してシリコン基板上に塗布した後、100℃の温度の乾燥器で1時間乾燥させて、シリコン基板上に塗布膜を形成した。得られた塗布膜に、YAGレーザの4倍波（266nm、10mJ／cm^2、300ショット）を照射した。これにより、上記した実施例3と同様にルチル（TiO_2）薄膜が得られた。

【0024】〔実施例5〕テトラノルマルブトキシジルコニウムを2－メトキシエタノールに溶解させ、ジルコニウムと等モルのアセチルアセトンを2－メトキシエタノール溶液に添加し、さらに、ジルコニウムと等モルの水を含む0．1規定塩酸を2－メトキシエタノール溶液に添加し、溶液を加水分解させて、塗布液を調製した。この塗布液中の金属酸化物の固形分濃度は、3重量％となるようにした。この塗布液を、スピンコータ（2，000rpm×15秒）を使用してシリコン基板上に塗布した後、100℃の温度の乾燥器で1時間乾燥させて、シリコン基板上に塗布膜を形成した。得られた塗布膜に、ArFエキシマレーザ（193nm、25mJ／cm^2、100ショット）を照射した。これにより、立方晶のジルコニア（ZrO_2）薄膜が得られた。さらに、塗布膜にArFエキシマレーザを1，000ショット照射することにより、ジルコニアの高温相である単斜晶が認められた。得られた薄膜の薄膜X線回折パターンの変化を図3に示す。

【0025】〔実施例6〕ジルコニウムテトラアセチルアセトナートを、金属酸化物の固形分濃度が3重量％となるようにメタノールに溶解させて、塗布液を調製した。この塗布液を、スピンコータ（2，000rpm×15秒）を使用してシリコン基板上に塗布した後、湿度60％の雰囲気中に3時間放置し、その後に100℃の温度のオーブンで1時間乾燥させて、シリコン基板上に塗布膜を形成した。得られた塗布膜に、ArFエキシマレーザ（193nm、25mJ／cm^2、1，000ショット）を照射した。これにより、上記した実施例5と同様に立方晶および単斜晶のジルコニア（ZrO_2）薄膜が得られた。

【0026】〔比較例1～6〕上記した実施例1～6において得られた塗布膜（金属酸化物ゲル膜）を加熱処理することにより、結晶性の金属酸化物薄膜を作製した。このときのそれぞれの加熱処理温度と得られた結晶相を表1にまとめて示す。

【0027】

【表1】

	加熱処理温度（℃）	結晶相
比較例1	４５０	Ta_2O_5
比較例2	４５０	Nb_2O_5
比較例3	４００ ７００	アナターゼ ルチル単相
比較例4	５００ ７００	アナターゼ ルチル単相
比較例5	５００ ８００	立方晶ジルコニア 単斜晶ジルコニア
比較例6	５００	立方晶ジルコニア

【００２８】表１から分かるように、結晶性の金属酸化物薄膜を得るためには、４００℃以上の温度での加熱処理が必要であった。特に、実施例３〜実施例６でそれぞれ得られたルチル単相膜や単斜晶ジルコニア膜を得るためには、７００℃以上の温度での加熱処理が必要であった。

【００２９】なお、この発明は、上記実施例で示した遷移金属酸化物薄膜の形成に限定されるものではなく、上記以外の遷移金属酸化物薄膜を加熱処理なしで形成する場合にも適用可能であることは言うまでもない。このように、加熱処理を行わずに結晶性の遷移金属酸化物薄膜を形成することができるので、この発明の方法によると、従来方法では不可能であったプラスチックス等の耐熱性に劣る基板上に遷移金属酸化物薄膜を形成することができ、また、有機物を含む多層膜における遷移金属酸化物薄膜の形成も可能になる。

【００３０】

【発明の効果】請求項１ないし請求項３に係る発明の製造方法によると、結晶化した遷移金属酸化物の薄膜を室温付近の温度で得ることができる。したがって、プラスチックスなどの耐熱性の低い基板上にも、結晶性の遷移金属酸化物薄膜を形成することが可能である。また、この製造方法を実施するために、高価な製造設備を使用する必要は無く、従って製造コストを低く抑えることができ、また、成膜しようとする基体の形状や大きさに制約されることもない。

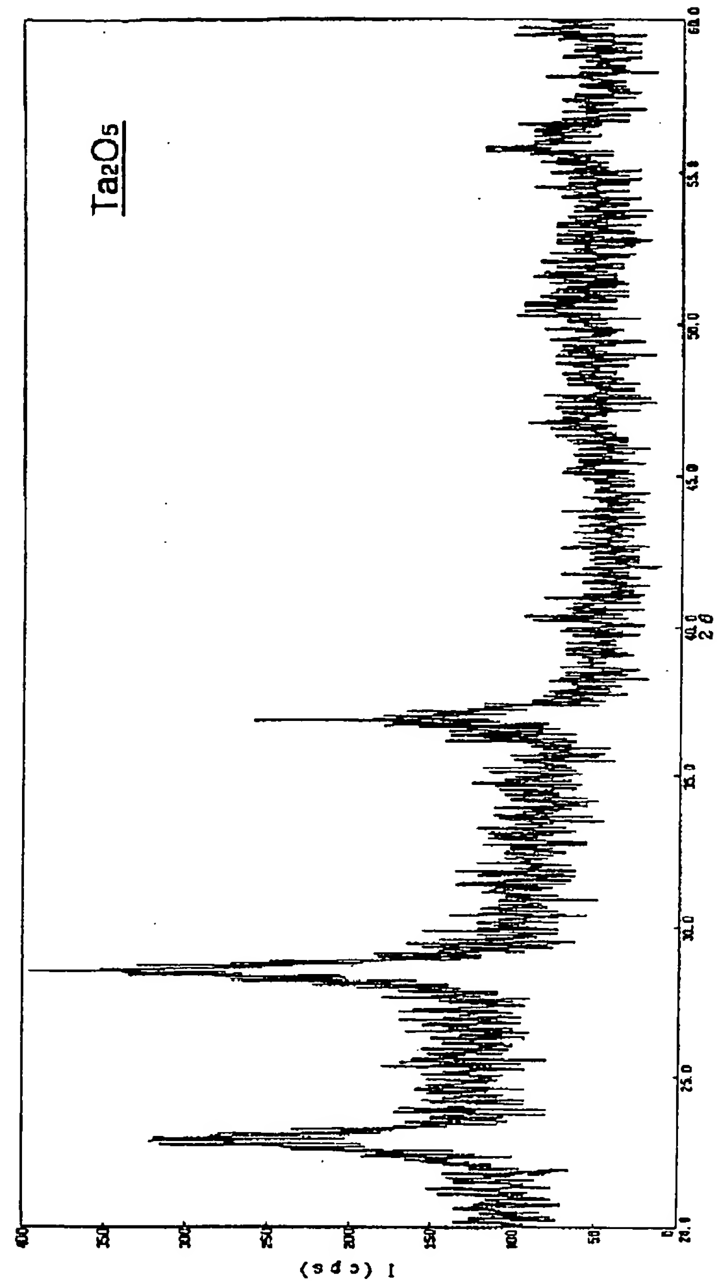
【図面の簡単な説明】

【図１】この発明に係る製造方法によって得られた酸化タンタル薄膜の薄膜Ｘ線回折パターンを示す図である。

【図２】同じく、この発明に係る製造方法によって得られたルチル薄膜の薄膜Ｘ線回折パターンの変化を示す図である。

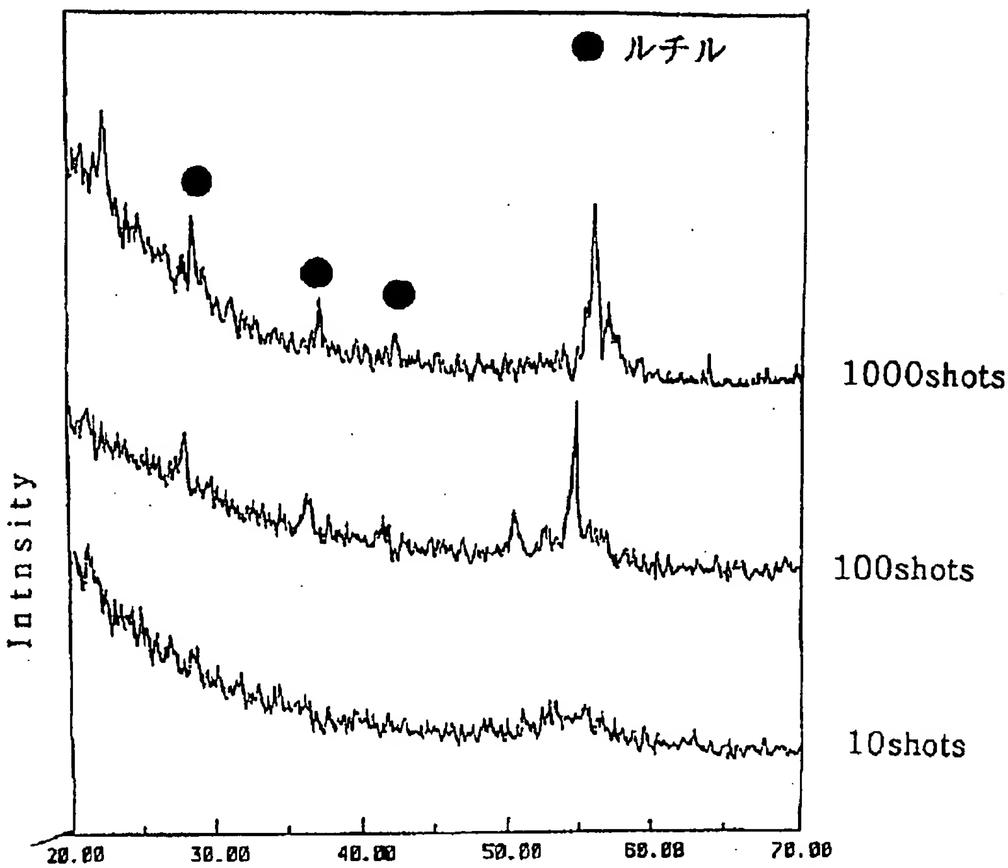
【図３】同じく、この発明に係る製造方法によって得られたジルコニア薄膜の薄膜Ｘ線回折パターンの変化を示す図である。

【図１】



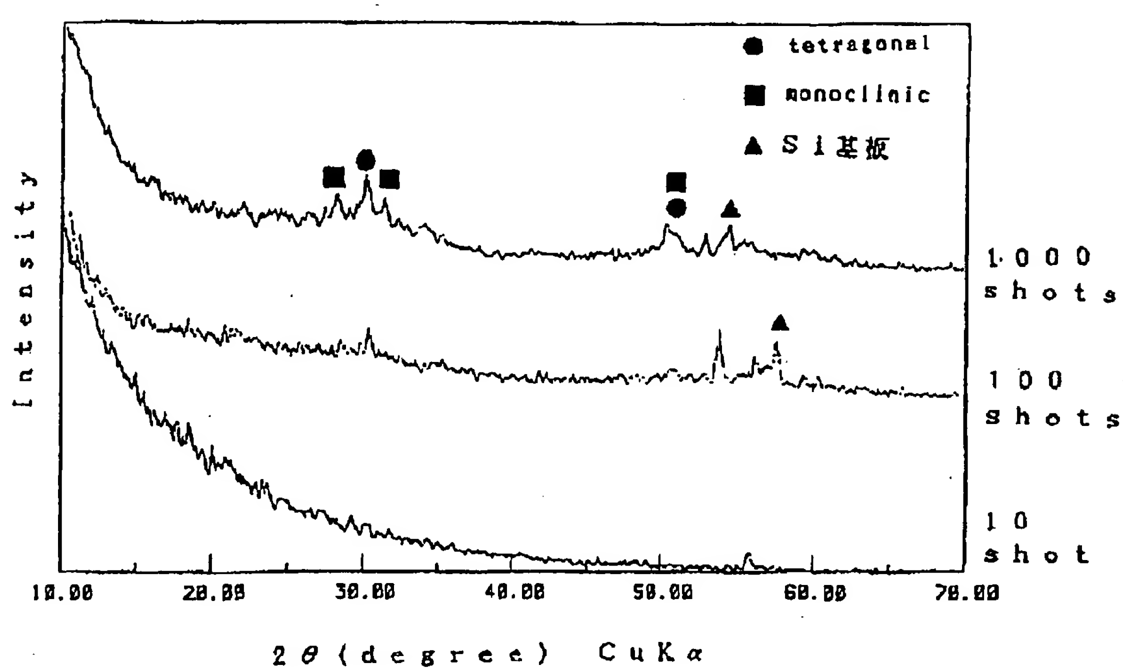
Ta2O5
I (cps)
2θ
0
50
100
150
200
250
300
350
400
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0

【図2】



● ルチル
1000shots
100shots
10shots
Intnsity
20.00
30.00
40.00
50.00
60.00
70.00

【図3】



● tetragonal
■ monoclinic
▲ Si基板
1000 shots
100 shots
10 shot
Intensity
10.00
20.00
30.00
40.00
50.00
60.00
70.00
2θ (degree) CuKα

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(71)Applicant : KANSAI SHINGIJUTSU KENKYUSHO:KK
(72)Inventor : ASAKUMA NAOKO
IMAI HIROAKI

(54) PRODUCTION OF METALLIC OXIDE THIN FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method capable of forming thin film of crystallized transition metal oxide even on a substrate low in heat resistance such as plastics, free from the need of the use of expensive producing equipment and free from restriction by the shape and size of a substrate to be film-formed.
SOLUTION: The surface of the object to be coated is coated with a precursory coating soln. of metallic oxide obtd. by using the alkoxide of salt of transition metal as a starting raw material to form coating film on the surface of the object to be coated, and thereafter, the coating film is irradiated with ultraviolet light of ≥360 nm wavelength to crystallize the transition metal oxide forming the coating film.

LEGAL STATUS

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[Date of registration]

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[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the metallic-oxide thin film which irradiates the ultraviolet radiation whose wavelength is 360nm or less to the application film, and is characterized by crystallizing the transition-metals oxide which forms the application film after applying the precursor application liquid of the metallic oxide obtained considering the alkoxide or salt of transition metals as a start raw material on the surface of a coated material and forming an application film in a coated material front face.

[Claim 2] The manufacture method of a metallic-oxide thin film according to claim 1 that transition metals are an IVa group element or Va group element.

[Claim 3] The manufacture method of a metallic-oxide thin film according to claim 1 or 2 that the light source of ultraviolet radiation irradiated to an application film is the 4 time wave of a high-pressure mercury lamp, a low-pressure mercury lamp, an ArF excimer laser, a KrF excimer laser, and an YAG laser or a 3 time wave, an excimer lamp, or synchrotron radiation.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to the manufacture method of the method of forming functional oxide thin films, such as electronic material, in the front face of substrates, such as glass, ceramics, a metal, and plastics, and the metallic-oxide thin film which forms the thin film of the transition-metals oxide crystallized without heat-treating especially.
[0002]
[Description of the Prior Art] The compound which has the electrical property which was excellent as a dielectric material, an electrical conducting material, a semiconductor material, etc. exists in a transition-metals oxide mostly. The thin film of these transition-metals oxide is manufactured by the sol-gel method, the spraying thermal decomposition method, the sputtering method, the MOCVD method, etc.
[0003] It is related with the manufacture method of the transition-metals oxide thin film by the sol-gel method. An anatase crystallizes a titania film at the temperature of 400 degrees C, and transferring to a rutile phase by heat-treating at the temperature of 800 more degrees C is known. for example, a zirconia film It crystallizes by heat-treating at the temperature of 700 degrees C (a ceramic industry association magazine, 94,823 (1986) references). a niobium-oxide film It crystallizes by heat-treating at the temperature of 400 degrees C (a KYATARISHISU toe day (Catalysis Today), 16,495 (1993) references). an iron-oxide film crystallizing to a gamma ferric oxide (HEGUMA -- tight) at the temperature to 450 degrees C, and heat-treating at the temperature of 450 more degrees C or more -- alpha-iron oxide -- transferring (a journal OBU material science (J. Mater.Sci.) --) Crystallizing 26,497 (1991) reference and a zinc-oxide film at the temperature of 400 degrees C or more (the Ceramic Society of Japan treatise magazine, 104, 296 (1991) references) is reported, respectively. Moreover, it is reported that thin films, such as an iron oxide, chromia, a titania, and a zirconia, are formed about the manufacture method of the transition-metals oxide thin film by the spraying thermal decomposition method by using various kinds of metal salts as a start raw material (tin solid films (Thin Solid Films), 77, 81 (1981) references).
[0004]
[Problem(s) to be Solved by the Invention] As described above, by the conventional method which forms the thin film of a transition-metals oxide with a general sol-gel method or a spraying part solution method, it is required to pyrolyze and remove the remains organic substance and a metal salt, and in order to crystallize a metallic oxide, the heat-treatment in an elevated temperature of 400 degrees C or more is indispensable as the result. For this reason, depending on the conventional method, the thin film of the crystallized transition-metals oxide was not able to be formed on the low base of thermal resistance, such as plastics.
[0005] Moreover, the sputtering method and the MOCVD method are based on a vacuum process, and, for this reason, have the trouble that an expensive manufacturing facility is required, and a manufacturing cost becomes high, and the configuration and size of a base which are going to form membranes have restrictions. Moreover, these methods also need heat-treatment of a substrate in many cases, in order to obtain a crystalline metallic-oxide thin film.
[0006] This invention is made in view of the above situations, can form the thin film of the crystallized transition-metals oxide also on the low base of thermal resistance, such as plastics, and aims at offering the manufacture method of a metallic-oxide thin film which is not restrained by the configuration or size of the base which the need of using an expensive manufacturing facility does not have, either, and is going to form membranes, either.
[0007]
[Means for Solving the Problem] Ultraviolet radiation was used for crystallizing the thin film of the transition-metals oxide gel formed by the sol-gel method as a means for attaining the above-mentioned purpose in this invention. That is, after invention concerning a claim 1 applies the precursor application liquid of the metallic oxide obtained considering the alkoxide or salt of transition metals as a start raw material on the surface of a coated material and forms an application film in a coated material front face, it irradiates the ultraviolet radiation whose wavelength is 360nm or less to the application film, and is characterized by crystallizing the transition-metals oxide which forms the application film.
[0008] By the manufacture method of invention concerning a claim 1, after applying the precursor application liquid of the metallic oxide obtained considering the alkoxide or salt of transition metals as a start raw material on the surface of a coated material and forming an application film, a transition-metals oxide is crystallized by irradiating the ultraviolet radiation whose

wavelength is 360nm or less to the application film. Therefore, since there is no need of performing heat-treatment in an elevated temperature for crystallization of a transition-metals oxide, it becomes possible to form the thin film of the crystallized transition-metals oxide also on a heat-resistant low base like plastics. In addition, although the mechanism of crystallization of the transition-metals oxide by irradiation of ultraviolet radiation is not clear, a thin film absorbs ultraviolet radiation, an atomic rearrangement is advanced by the energy and it is thought that a transition-metals oxide crystallizes.
[0009] Invention concerning a claim 2 is characterized by transition metals being an IVa group element or Va group element in the manufacture method according to claim 1.
[0010] Invention concerning a claim 3 is characterized by using the 4 time wave or 3 time wave of a high-pressure mercury lamp, a low-pressure mercury lamp, an ArF excimer laser, a KrF excimer laser, and an YAG laser, an excimer lamp, or synchrotron radiation in the manufacture method according to claim 1 or 2 as the light source of ultraviolet radiation irradiated to the thin film of metallic-oxide gel. Even if it uses only one kind of thing, you may use the light source combining two or more sorts of things.
[0011]
[Embodiments of the Invention] Hereafter, the suitable operation gestalt of this invention is explained.
[0012] By the manufacture method of the metallic-oxide thin film concerning this invention, the precursor application liquid (sol) of a metallic oxide is first prepared by using the alkoxide or salt of transition metals as a start raw material. Transition metals are for example, an IVa group element or Va group element. Especially the manufacture method of application liquid is so desirable that [when an application film (gel film) is formed, so that the remains organic substance in a film decreases, and] the crystallization temperature of the gel film by heat-treatment becomes low, although not limited. The manufacture method of application liquid is explained below.
[0013] As a metal alkoxide used as a start raw material, that whose carbon numbers of an alkoxyl group are 1-5 is used, and the thing of 2-4 is more preferably used for the carbon number of an alkoxyl group. Moreover, as a metal salt, organic acid chloride, such as mineral salt, such as a nitrate and a chloride, and an acetic acid, and the salt of beta-diketones, such as acetylacetonato, are used.
[0014] As a solvent in which a metal alkoxide or a metal salt is dissolved, aromatic series, such as acid amides, such as the cyclo ether, such as ketones, such as organic-acid ester, such as alcohols, such as a methanol, ethanol, propanol, and a butanol, and ethyl acetate, an acetonitrile, an acetone, and a methyl ethyl ketone, a tetrapod hydra furan (THF), and a dioxane, a formamide (FA), and N.N-dimethylformamide (DMF), a hydrocarbon, and toluene, etc. are used.
[0015] Moreover, you may make it contained in the solution containing a metal alkoxide for the purpose of stabilization of beta-diketone (RCOCH2COR';R and R' is an alkyl group or an alkoxyl group) which is a polydent compound, alkoxy alcohol, an alkanolamine, glycols, a glycerol, etc. of an alkoxide. As a beta-diketone, malonic esters, such as acetoacetic ester, such as an acetylacetone, an ethyl acetoacetate, and a methyl acetoacetate, and a diethyl malonate, etc. are used. As alkoxy alcohol, a 2-methoxyethanol, the 2-ethoxyethanol, 2-methoxy-2-propanol, etc. are used. A monoethanolamine, a diethanolamine, a triethanolamine, etc. are used as an alkanolamine. As glycols, monoalkyl ether and acetic ester of ethylene glycol, a diethylene glycol, a triethylene glycol and propylene glycols, or these compounds are used. These compounds are used independently, or are used together, and the kind is selected by a metal kind and the kind of alkoxyl group. Moreover, as for these compounds, it is desirable to contain the twice many 0.1-mol amount of twice - 1.5 mols as this of an alkoxide. In addition, alkoxy alcohols can also be used as a solvent.
[0016] The twice as many 0.05-mol twice - two-mol water of a metal alkoxide or a metal salt as this is used for hydrolysis of the solution containing a metal alkoxide or a metal salt, and twice as many 0.5-mol twice - 1.5-mol water as this is more preferably used for it. You may make it use an acid catalyst and/or a base catalyst for this hydrolysis, and organic acids, such as mineral acids, such as a hydrochloric acid, and an acetic acid, are preferably used for it. In addition, the diluted solution of an alkoxide is used depending on the kind of alkoxide. Moreover, when a metal salt is used as a start raw material, a reaction with the solvent of an alcoholic system is used effectively.
[0017] If the precursor application liquid (sol) of a metallic oxide is prepared by hydrolysis of the solution containing the alkoxide or salt of transition metals, the application liquid will be applied on the surface of a substrate, it will be dried, and an application film (metallic-oxide gel film) will be formed in a substrate front face. Especially the method of application of application liquid is not limited, but the dip coating method usually performed, the spin coat method, the flow coat method, the bar coat method, an ultrasonic atomizing process, etc. are used. In addition, the crystallization temperature at the time of heat-treating is so desirable that there is little remains organic amount of resources in the film as a gel film obtained at this time as described above as a low.
[0018] If an application film is formed in a substrate front face, the ultraviolet radiation whose wavelength is 360nm or less will be irradiated to the application film. If irradiation to the ultraviolet radiation whose wavelength is 360nm or less is possible as the light source of ultraviolet radiation, although it will be used according to the metallic-oxide thin film which does not ask the kind but is made into the purpose, choosing suitably, a high-pressure mercury lamp, a low-pressure mercury lamp, an excimer lamp, an ArF excimer laser, a KrF excimer laser, a 4 times many YAG laser [as this] wave or a 3 time wave, synchrotron radiation, etc. are used, for example. Moreover, it is also possible to use it combining two or the thing beyond it among these light sources. It is also possible to heat a substrate, to put a substrate under reduced pressure, or to control atmosphere (an oxidizing atmosphere or non-oxidizing atmosphere) according to the purpose, in the case of the ultraviolet radiation irradiation to this application film. Moreover, the irradiation intensity and the shots per hour of ultraviolet

radiation are suitably chosen according to the kind of application film, composition, etc. By irradiating ultraviolet radiation to an application film, the metallic-oxide gel which forms the application film is crystallized, and the thin film of a transition-metals oxide is formed on the surface of a substrate.

[0019]

[Example] Next, the example which applied this invention concretely is explained.

[0020] [Example 1] The pentaethoxy tantalum was dissolved in ethanol so that the solid-content concentration of a metallic oxide might become 3 % of the weight, and application liquid was prepared. After applying this application liquid on a silica substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silica substrate. The ArF excimer laser (193nm, 2,300 shot of 25 mJ/cm) was irradiated at the obtained application film. Thereby, the crystalline tantalum oxide (Ta 2O5) thin film was obtained. The thin film X diffraction pattern of the obtained thin film is shown in drawing 1 .

[0021] [Example 2] Pentaethoxy niobium was dissolved in ethanol so that the solid-content concentration of a metallic oxide might become 3 % of the weight, and application liquid was prepared. After applying this application liquid on a silica substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silica substrate. The ArF excimer laser (193nm, 2,300 shot of 25 mJ/cm) was irradiated at the obtained application film. Thereby, the crystalline niobium-oxide (Nb 2O5) thin film was obtained.

[0022] [Example 3] Dissolved tetraisopropoxy titanium in the 2-methoxyethanol, added the 0.1 convention hydrochloric acid containing the water of mols [titanium] in the 2-methoxyethanol solution, the solution was made to understand an added water part, and application liquid was prepared. It was made for the solid-content concentration of the metallic oxide in this application liquid to become 3 % of the weight. After applying this application liquid on a silicon substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silicon substrate. The 4 time wave (266nm, 10 mJ/cm2) of an YAG laser was changed, and the irradiation shots per hour was irradiated on it at the obtained application film. Thereby, the rutile (TiO2) thin film was obtained. When an irradiation shots per hour was 100 shots, the rutile diffraction peak was accepted. Change of the thin film X diffraction pattern of the obtained thin film is shown in drawing 2 .

[0023] [Example 4] It added to dehydrated ethanol so that the solid-content concentration of a metallic oxide might become 3 % of the weight, and a titanium tetrachloride will be agitated for one day, and was dissolved, and application liquid was prepared. After applying this application liquid on a silicon substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silicon substrate. The 4 time wave (266nm, 2,300 shot of 10 mJ/cm) of an YAG laser was irradiated at the obtained application film. Thereby, the rutile (TiO2) thin film was obtained like the above-mentioned example 3.

[0024] [Example 5] Dissolved tetra-N-butoxyzirconium in the 2-methoxyethanol, added the acetylacetone of mols [zirconium] in the 2-methoxyethanol solution, added the 0.1 convention hydrochloric acid containing the water of mols [zirconium] in the 2-methoxyethanol solution further, the solution was made to understand an added water part, and application liquid was prepared. It was made for the solid-content concentration of the metallic oxide in this application liquid to become 3 % of the weight. After applying this application liquid on a silicon substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silicon substrate. The ArF excimer laser (193nm, 2,100 shot of 25 mJ/cm) was irradiated at the obtained application film. Thereby, the cubic zirconia (ZrO2) thin film was obtained. Furthermore, when 1,000 shots irradiated an ArF excimer laser at an application film, the monoclinic system which is the parent phase of a zirconia was accepted. Change of the thin film X diffraction pattern of the obtained thin film is shown in drawing 3 .

[0025] [Example 6] Zirconium tetrapod acetylacetonato was dissolved in the methanol so that the solid-content concentration of a metallic oxide might become 3 % of the weight, and application liquid was prepared. After applying this application liquid on a silicon substrate using a spin coater (2,000rpmx 15 seconds), left it in the atmosphere of 60% of humidity for 3 hours, it was made to dry in oven with a temperature of 100 degrees C after that for 1 hour, and the application film was formed on the silicon substrate. The ArF excimer laser (193nm, 2 or 1,000 shot of 25 mJ/cm) was irradiated at the obtained application film. Thereby, the zirconia (ZrO2) thin film of a cubic and monoclinic system was obtained like the above-mentioned example 5.

[0026] [Examples 1-6 of comparison] The crystalline metallic-oxide thin film was produced by heat-treating the application film (metallic-oxide gel film) obtained in the above-mentioned examples 1-6. Each heat-treatment temperature at this time and the obtained crystal phase are collectively shown in Table 1.

[0027]

[Table 1]

	加熱処理温度（℃）	結　晶　相
比較例 1	４５０	Ta_2O_5
比較例 2	４５０	Nb_2O_5
比較例 3	４００ ７００	アナターゼ ルチル単相
比較例 4	５００ ７００	アナターゼ ルチル単相
比較例 5	５００ ８００	立方晶ジルコニア 単斜晶ジルコニア
比較例 6	５００	立方晶ジルコニア

[0028] As shown in Table 1, in order to obtain a crystalline metallic-oxide thin film, heat-treatment at the temperature of 400 degrees C or more was required. In order to obtain the rutile single phase film and monoclinic system zirconia film which were especially obtained in the example 3 - the example 6, respectively, heat-treatment at the temperature of 700 degrees C or more was required.
[0029] In addition, this invention cannot be overemphasized by that it can apply when it is not limited to formation of the transition-metals oxide thin film shown in the above-mentioned example and forms transition-metals oxide thin films other than the above without heat-treatment. Thus, since a crystalline transition-metals oxide thin film can be formed without heat-treating, according to the method of this invention, by the conventional method, formation of the transition-metals oxide thin film in the multilayer which can form a transition-metals oxide thin film on the substrate inferior to thermal resistance, such as impossible plastics, and contains the organic substance is also attained.
[0030]
[Effect of the Invention] According to the manufacture method of invention concerning a claim 1 or a claim 3, the thin film of the crystallized transition-metals oxide can be obtained at the temperature near a room temperature. Therefore, it is possible to form a crystalline transition-metals oxide thin film also on the low substrate of thermal resistance, such as plastics. Moreover, in order to enforce this manufacture method, the need of using an expensive manufacturing facility is not restrained by the configuration or size of a base which there are not, can hold down a manufacturing cost low, and are going to form membranes.

[Translation done.]

TECHNICAL FIELD

[The technical field to which invention belongs] This invention relates to the manufacture method of the method of forming functional oxide thin films, such as electronic material, in the front face of substrates, such as glass, ceramics, a metal, and plastics, and the metallic-oxide thin film which forms the thin film of the transition-metals oxide crystallized without heat-treating especially.

[Translation done.]

PRIOR ART

[Description of the Prior Art] The compound which has the electrical property which was excellent as a dielectric material, an electrical conducting material, a semiconductor material, etc. exists in a transition-metals oxide mostly. The thin film of these transition-metals oxide is manufactured by the sol-gel method, the spraying thermal decomposition method, the sputtering method, the MOCVD method, etc.

[0003] It is related with the manufacture method of the transition-metals oxide thin film by the sol-gel method. An anatase crystallizes a titania film at the temperature of 400 degrees C, and transferring to a rutile phase by heat-treating at the temperature of 800 more degrees C is known. for example, a zirconia film It crystallizes by heat-treating at the temperature of 700 degrees C (a ceramic industry association magazine, 94,823 (1986) references). a niobium-oxide film It crystallizes by heat-treating at the temperature of 400 degrees C (a KYATARISHISU toe day (Catalysis Today), 16,495 (1993) references). an iron-oxide film crystallizing to a gamma ferric oxide (HEGUMA -- tight) at the temperature to 450 degrees C, and heat-treating at the temperature of 450 more degrees C or more -- alpha-iron oxide -- transferring (a journal OBU material science (J. Mater.Sci.) --) Crystallizing 26,497 (1991) reference and a zinc-oxide film at the temperature of 400 degrees C or more (the Ceramic Society of Japan treatise magazine, 104, 296 (1991) references) is reported, respectively. Moreover, it is reported that thin films, such as an iron oxide, chromia, a titania, and a zirconia, are formed about the manufacture method of the transition-metals oxide thin film by the spraying thermal decomposition method by using various kinds of metal salts as a start raw material (tin solid films (Thin Solid Films), 77, 81 (1981) references).

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] According to the manufacture method of invention concerning a claim 1 or a claim 3, the thin film of the crystallized transition-metals oxide can be obtained at the temperature near a room temperature. Therefore, it is possible to form a crystalline transition-metals oxide thin film also on the low substrate of thermal resistance, such as plastics. Moreover, in order to enforce this manufacture method, the need of using an expensive manufacturing facility is not restrained by the configuration or size of a base which there are not, can hold down a manufacturing cost low, and are going to form membranes.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] As described above, by the conventional method which forms the thin film of a transition-metals oxide with a general sol-gel method or a spraying part solution method, it is required to pyrolyze and remove the remains organic substance and a metal salt, and in order to crystallize a metallic oxide, the heat-treatment in an elevated temperature of 400 degrees C or more is indispensable as the result. For this reason, depending on the conventional method, the thin film of the crystallized transition-metals oxide was not able to be formed on the low base of thermal resistance, such as plastics.
[0005] Moreover, the sputtering method and the MOCVD method are based on a vacuum process, and, for this reason, have the trouble that an expensive manufacturing facility is required, and a manufacturing cost becomes high, and the configuration and size of a base which are going to form membranes have restrictions. Moreover, these methods also need heat-treatment of a substrate in many cases, in order to obtain a crystalline metallic-oxide thin film.
[0006] This invention is made in view of the above situations, can form the thin film of the crystallized transition-metals oxide also on the low base of thermal resistance, such as plastics, and aims at offering the manufacture method of a metallic-oxide thin film which is not restrained by the configuration or size of the base which the need of using an expensive manufacturing facility does not have, either, and is going to form membranes, either.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] Ultraviolet radiation was used for crystallizing the thin film of the transition-metals oxide gel formed by the sol-gel method as a means for attaining the above-mentioned purpose in this invention. That is, after invention concerning a claim 1 applies the precursor application liquid of the metallic oxide obtained considering the alkoxide or salt of transition metals as a start raw material on the surface of a coated material and forms an application film in a coated material front face, it irradiates the ultraviolet radiation whose wavelength is 360nm or less to the application film, and is characterized by crystallizing the transition-metals oxide which forms the application film.
[0008] By the manufacture method of invention concerning a claim 1, after applying the precursor application liquid of the metallic oxide obtained considering the alkoxide or salt of transition metals as a start raw material on the surface of a coated material and forming an application film, a transition-metals oxide is crystallized by irradiating the ultraviolet radiation whose wavelength is 360nm or less to the application film. Therefore, since there is no need of performing heat-treatment in an elevated temperature for crystallization of a transition-metals oxide, it becomes possible to form the thin film of the crystallized transition-metals oxide also on a heat-resistant low base like plastics. In addition, although the mechanism of crystallization of the transition-metals oxide by irradiation of ultraviolet radiation is not clear, a thin film absorbs ultraviolet radiation, an atomic rearrangement is advanced by the energy and it is thought that a transition-metals oxide crystallizes.
[0009] Invention concerning a claim 2 is characterized by transition metals being an IVa group element or Va group element in the manufacture method according to claim 1.
[0010] Invention concerning a claim 3 is characterized by using the 4 time wave or 3 time wave of a high-pressure mercury lamp, a low-pressure mercury lamp, an ArF excimer laser, a KrF excimer laser, and an YAG laser, an excimer lamp, or synchrotron radiation in the manufacture method according to claim 1 or 2 as the light source of ultraviolet radiation irradiated to the thin film of metallic-oxide gel. Even if it uses only one kind of thing, you may use the light source combining two or more sorts of things.
[0011]
[Embodiments of the Invention] Hereafter, the suitable operation form of this invention is explained.
[0012] By the manufacture method of the metallic-oxide thin film concerning this invention, the precursor application liquid (sol) of a metallic oxide is first prepared by using the alkoxide or salt of transition metals as a start raw material. Transition metals are for example, an IVa group element or Va group element. Especially the manufacture method of application liquid is so desirable that [when an application film (gel film) is formed, so that the remains organic substance in a film decreases, and] the crystallization temperature of the gel film by heat-treatment becomes low, although not limited. The manufacture method of application liquid is explained below.
[0013] As a metal alkoxide used as a start raw material, that whose carbon numbers of an alkoxyl group are 1-5 is used, and the thing of 2-4 is more preferably used for the carbon number of an alkoxyl group. Moreover, as a metal salt, organic acid chloride, such as mineral salt, such as a nitrate and a chloride, and an acetic acid, and the salt of beta-diketones, such as acetylacetonato, are used.
[0014] As a solvent in which a metal alkoxide or a metal salt is dissolved, aroma groups, such as acid amides, such as the cyclo ether, such as ketones, such as organic-acid ester, such as alcohols, such as a methanol, ethanol, propanol, and a butanol, and ethyl acetate, an acetonitrile, an acetone, and a methyl ethyl ketone, a tetrapod hydra furan (THF), and a dioxane, a formamide (FA), and N.N-dimethylformamide (DMF), a hydrocarbon, and toluene, etc. are used.
[0015] Moreover, you may make it contained in the solution containing a metal alkoxide for the purpose of stabilization of beta-diketone (RCOCH2COR';R and R' is an alkyl group or an alkoxyl group) which is a polydent compound, alkoxy alcohol, an alkanolamine, glycols, a glycerol, etc. of an alkoxide. As a beta-diketone, malonic esters, such as acetoacetic ester, such as an acetylacetone, an ethyl acetoacetate, and a methyl acetoacetate, and a diethyl malonate, etc. are used. As alkoxy alcohol, a 2-methoxyethanol, a 2-ethoxyethanol, 2-methoxy-2-propanol, etc. are used. A monoethanolamine, a diethanolamine, a triethanolamine, etc. are used as an alkanolamine. As glycols, monoalkyl ether and acetic ester of ethylene glycol, a diethylene glycol, a triethylene glycol and propylene glycols, or these compounds are used. These compounds are used independently, or are used together, and the kind is selected by a metal kind and the kind of alkoxyl group. Moreover, as for these compounds, it is desirable to contain the twice many 0.1-mol amount of twice - 1.5 mols as this of an alkoxide. In addition, alkoxy alcohols can also be used as a solvent.
[0016] The twice as many 0.05-mol twice - two-mol water of a metal alkoxide or a metal salt as this is used for hydrolysis of

the solution containing a metal alkoxide or a metal salt, and twice as many 0.5-mol twice - 1.5-mol water as this is more preferably used for it. You may make it use an acid catalyst and/or a base catalyst for this hydrolysis, and organic acids, such as mineral acids, such as a hydrochloric acid, and an acetic acid, are preferably used for it. In addition, the diluted solution of an alkoxide is used depending on the kind of alkoxide. Moreover, when a metal salt is used as a start raw material, a reaction with the solvent of an alcoholic system is used effectively.

[0017] If the precursor application liquid (sol) of a metallic oxide is prepared by hydrolysis of the solution containing the alkoxide or salt of transition metals, the application liquid will be applied on the surface of a substrate, it will be dried, and an application film (metallic-oxide gel film) will be formed in a substrate front face. Especially the method of application of application liquid is not limited, but the dip coating method usually performed, the spin coat method, the flow coat method, the bar coat method, an ultrasonic atomizing process, etc. are used. In addition, as a gel film obtained at this time, it is so desirable that [as described above, so that there is little remains organic amount of resources in the film, and] the crystallization temperature at the time of heat-treating is low.

[0018] If an application film is formed in a substrate front face, the ultraviolet radiation whose wavelength is 360nm or less will be irradiated to the application film. If irradiation to the ultraviolet radiation whose wavelength is 360nm or less is possible as the light source of ultraviolet radiation, although it will be used according to the metallic-oxide thin film which does not ask the kind but is made into the purpose, choosing suitably, a high-pressure mercury lamp, a low-pressure mercury lamp, an excimer lamp, an ArF excimer laser, a KrF excimer laser, a 4 times many YAG laser [as this] wave or a 3 time wave, synchrotron radiation, etc. are used, for example. Moreover, it is also possible to use it combining two or the thing beyond it among these light sources. It is also possible to heat a substrate, to put a substrate under reduced pressure, or to control atmosphere (an oxidizing atmosphere or non-oxidizing atmosphere) according to the purpose, in the case of the ultraviolet radiation irradiation to this application film. Moreover, the irradiation intensity and the shots per hour of ultraviolet radiation are suitably chosen according to the kind of application film, composition, etc. By irradiating ultraviolet radiation to an application film, the metallic-oxide gel which forms the application film is crystallized, and the thin film of a transition-metals oxide is formed on the surface of a substrate.

[Translation done.]

EXAMPLE

[Example] Next, the example which applied this invention concretely is explained.
[0020] [Example 1] The pentaethoxy tantalum was dissolved in ethanol so that the solid-content concentration of a metallic oxide might become 3 % of the weight, and application liquid was prepared. After applying this application liquid on a silica substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silica substrate. The ArF excimer laser (193nm, 2,300 shot of 25 mJ/cm) was irradiated at the obtained application film. Thereby, the crystalline tantalum oxide (Ta 2O5) thin film was obtained. The thin film X diffraction pattern of the obtained thin film is shown in drawing 1.
[0021] [Example 2] Pentaethoxy niobium was dissolved in ethanol so that the solid-content concentration of a metallic oxide might become 3 % of the weight, and application liquid was prepared. After applying this application liquid on a silica substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silica substrate. The ArF excimer laser (193nm, 2,300 shot of 25 mJ/cm) was irradiated at the obtained application film. Thereby, the crystalline niobium-oxide (Nb 2O5) thin film was obtained.
[0022] [Example 3] Dissolved tetraisopropoxy titanium in the 2-methoxyethanol, added the decinormal hydrochloric acid containing the water of mols [titanium] in the 2-methoxyethanol solution, the solution was made to understand an added water part, and application liquid was prepared. It was made for the solid-content concentration of the metallic oxide in this application liquid to become 3 % of the weight. After applying this application liquid on a silicon substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silicon substrate. The 4 time wave (266nm, 10 mJ/cm2) of an YAG laser was changed, and the irradiation shots per hour was irradiated on it at the obtained application film. Thereby, the rutile (TiO2) thin film was obtained. When an irradiation shots per hour was 100 shots, the rutile diffraction peak was accepted. Change of the thin film X diffraction pattern of the obtained thin film is shown in drawing 2.
[0023] [Example 4] It added to dehydrated ethanol so that the solid-content concentration of a metallic oxide might become 3 % of the weight, and a titanium tetrachloride will be agitated for one day, and was dissolved, and application liquid was prepared. After applying this application liquid on a silicon substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silicon substrate. The 4 time wave (266nm, 2,300 shot of 10 mJ/cm) of an YAG laser was irradiated at the obtained application film. Thereby, the rutile (TiO2) thin film was obtained like the above-mentioned example 3.
[0024] [Example 5] Dissolved tetra-N-butoxyzirconium in the 2-methoxyethanol, added the acetylacetone of mols [zirconium] in the 2-methoxyethanol solution, added the decinormal hydrochloric acid containing the water of mols [zirconium] in the 2-methoxyethanol solution further, the solution was made to understand an added water part, and application liquid was prepared. It was made for the solid-content concentration of the metallic oxide in this application liquid to become 3 % of the weight. After applying this application liquid on a silicon substrate using a spin coater (2,000rpmx 15 seconds), it was made to dry with an oven with a temperature of 100 degrees C for 1 hour, and the application film was formed on the silicon substrate. The ArF excimer laser (193nm, 2,100 shot of 25 mJ/cm) was irradiated at the obtained application film. Thereby, the cubic zirconia (ZrO2) thin film was obtained. Furthermore, when 1,000 shots irradiated an ArF excimer laser at an application film, the monoclinic system which is the parent phase of a zirconia was accepted. Change of the thin film X diffraction pattern of the obtained thin film is shown in drawing 3.
[0025] [Example 6] Zirconium tetrapod acetylacetonato was dissolved in the methanol so that the solid-content concentration of a metallic oxide might become 3 % of the weight, and application liquid was prepared. After applying this application liquid on a silicon substrate using a spin coater (2,000rpmx 15 seconds), left it in the atmosphere of 60% of humidity for 3 hours, it was made to dry in oven with a temperature of 100 degrees C after that for 1 hour, and the application film was formed on the silicon substrate. The ArF excimer laser (193nm, 2 or 1,000 shot of 25 mJ/cm) was irradiated at the obtained application film. Thereby, the zirconia (ZrO2) thin film of a cubic and monoclinic system was obtained like the above-mentioned example 5.
[0026] [Examples 1-6 of comparison] The crystalline metallic-oxide thin film was produced by heat-treating the application film (metallic-oxide gel film) obtained in the above-mentioned examples 1-6. Each heat-treatment temperature at this time and the obtained crystal phase are collectively shown in Table 1.

[0027]
[Table 1]

	加熱処理温度（℃）	結晶相
比較例1	450	Ta_2O_5
比較例2	450	Nb_2O_5
比較例3	400 700	アナターゼ ルチル単相
比較例4	500 700	アナターゼ ルチル単相
比較例5	500 800	立方晶ジルコニア 単斜晶ジルコニア
比較例6	500	立方晶ジルコニア

[0028] As shown in Table 1, in order to obtain a crystalline metallic-oxide thin film, heat-treatment at the temperature of 400 degrees C or more was required. In order to obtain the rutile single phase film and monoclinic system zirconia film which were especially obtained in the example 3 - the example 6, respectively, heat-treatment at the temperature of 700 degrees C or more was required.
[0029] In addition, this invention cannot be overemphasized by that it can apply when it is not limited to formation of the transition-metals oxide thin film shown in the above-mentioned example and forms transition-metals oxide thin films other than the above without heat-treatment. Thus, since a crystalline transition-metals oxide thin film can be formed without heat-treating, according to the method of this invention, by the conventional method, formation of the transition-metals oxide thin film in the multilayer which can form a transition-metals oxide thin film on the substrate inferior to thermal resistance, such as impossible plastics, and contains the organic substance is also attained.

[Translation done.]

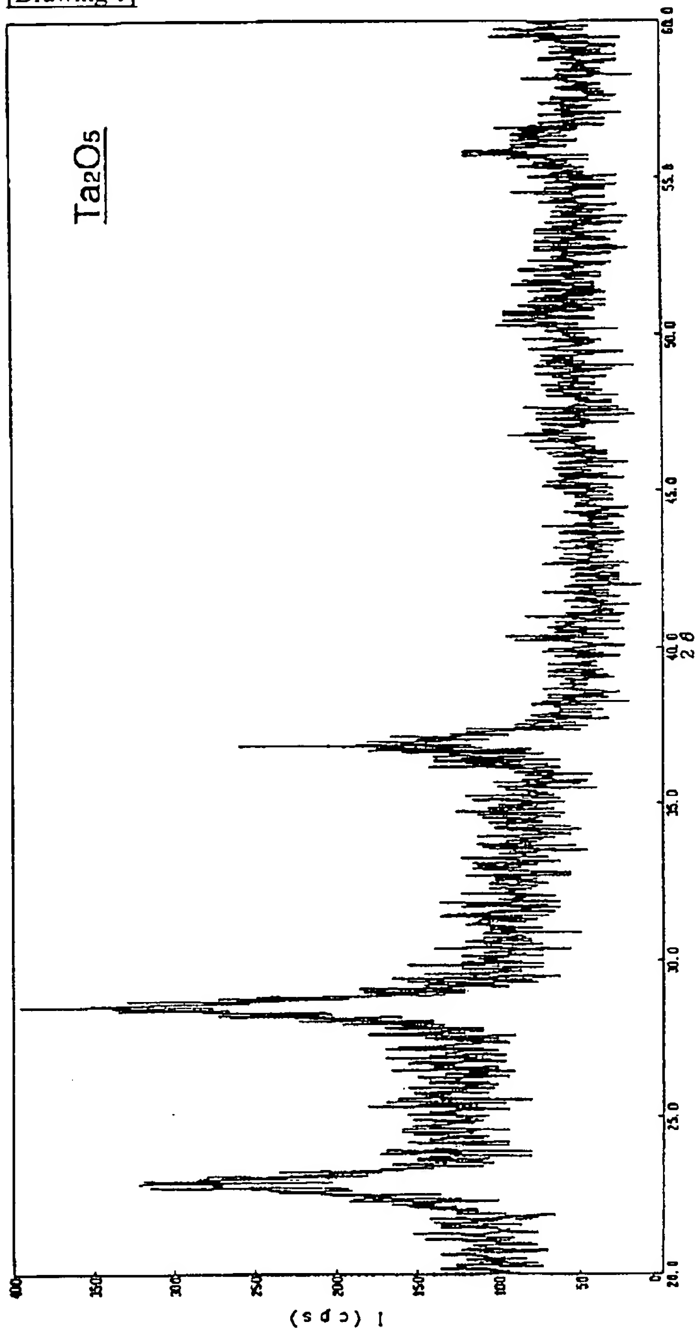
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the thin film X diffraction pattern of the tantalum oxide thin film obtained by the manufacture method concerning this invention.
[Drawing 2] It is drawing showing change of the thin film X diffraction pattern of the rutile thin film similarly obtained by the manufacture method concerning this invention.
[Drawing 3] It is drawing showing change of the thin film X diffraction pattern of the zirconia thin film similarly obtained by the manufacture method concerning this invention.

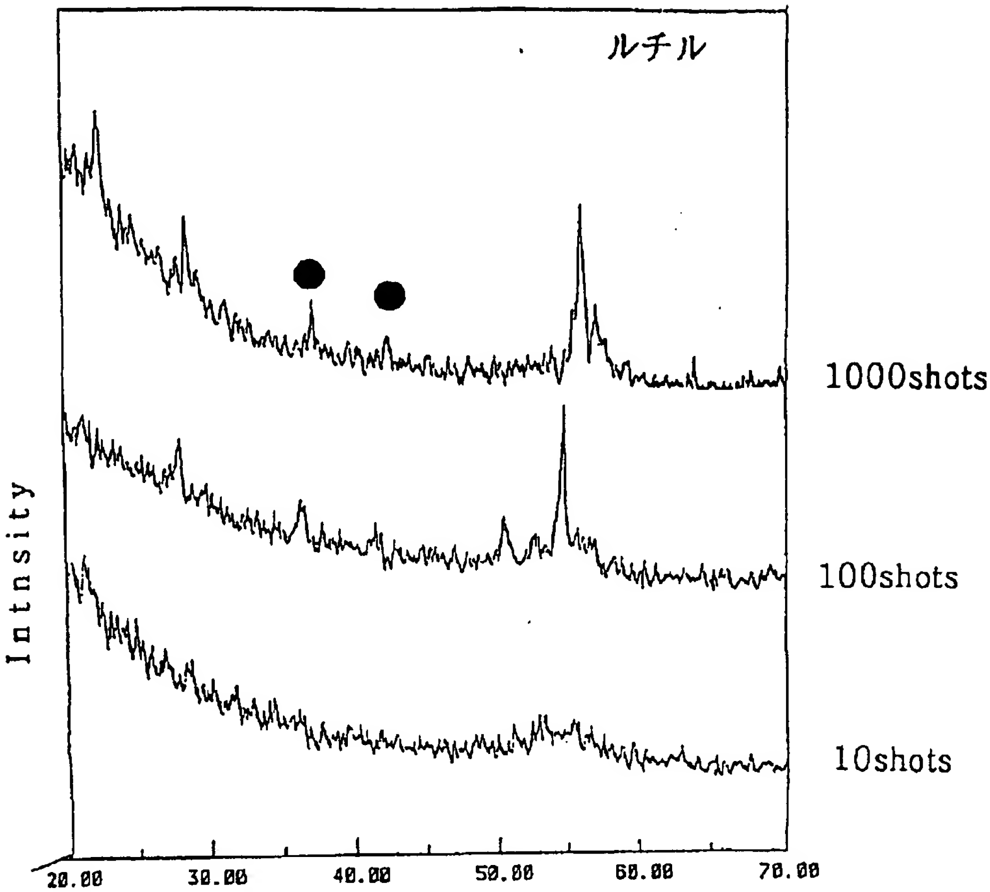
[Translation done.]

DRAWINGS

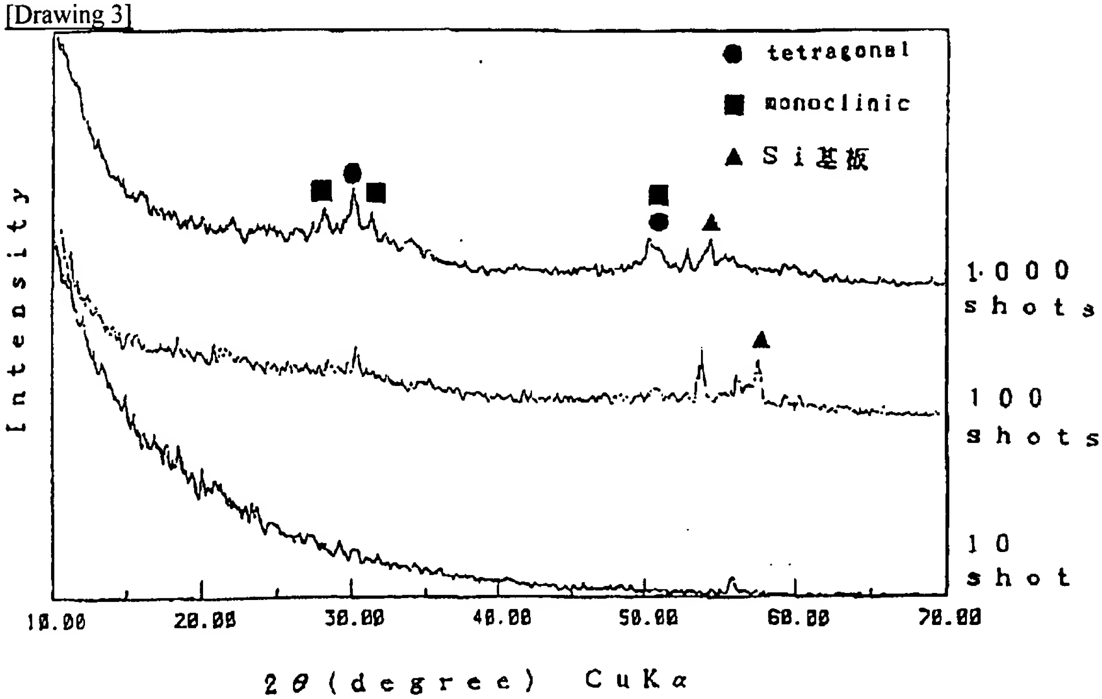
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]